UNIT 12

REACTIONS OF AROMATIC COMPOUNDS - II

Structure

12.1 INTRODUCTION

In the last unit, Unit 11, we have learnt some important reactions of aromatic compounds. There are two main types of substitution reactions in aromatic compounds i.e. i) substitution reactions at aromatic ring and ii) substitution reactions at the side chain of aromatic ring. In that unit, we have also discussed electrophilic substitution reactions on benzene ring. In this unit, we will explain the effect of substituents on reactivity and orientation of aromatic compounds. In the next section we will consider the meaning of *ortho, para* and *meta* directing activators/deactivators. In addition to this, we will study the substitution reactions of side chain of aromatic compounds. You will notice that the substitution of side chain follows free radical mechanism while substitution at ring carbon follows ionic mechanism. In the last section, we will discuss the oxidation of side chain of aromatic compounds.

Expected Learning Outcomes

After studying this unit, you should be able to:

- explain the effect of substituents on reactivity;
- explain the effect of substituents on orientation;

- ❖ state the concept of *ortho, para and meta* directing activator/deactivator;
- ❖ describe the substitution in the side chain of aromatic compounds; and
- ❖ explain the oxidation reactions of the side chain.

12.2 EFFECT OF SUBSTITUENTS ON REACTIVITY AND ORIENTATION

Benzene forms only one monosubstituted product by the electrophilic substitution. Let us see what happens when we carry out an electrophilic substitution on a substituted benzene. Studies have shown that the substituents effect the reactivity and the orientation in the benzene ring. Three possible disubstituted products, viz., *ortho*, *para* and *meta* can result. These three products are not formed at random; rather, a given substituent already attached to the benzene ring usually directs the position of the second substituent. There are two types of substituents – one is electron-donating groups, such as $-NR_2$, $-OH$, $-OR$, $-NHCOR$, and alkyl groups and other is electron-withdrawing groups which include halogens, $-CHO$, $-COR$, $-COOR$, $-CN$, $-NO_2$, $-\overset{+}{N}R_3$ etc..

Now we will study the effect of substituents on reactivity and orientation.

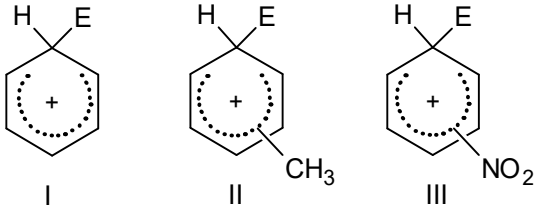
12.2.1 Effect of Substituents on Reactivity

To compare the rates of electrophilic substitution in benzene, methyl substituted benzene (methylbenzene or toluene) and nitro substituted benzene (nitrobenzene) are compared in a reaction, say nitration. It is found that nitration of methylbenzene (toluene) is more facile than benzene whereas nitration of nitrobenzene is more difficult than benzene. In other words, benzene ring seems to be activated in methylbenzene and deactivated in nitrobenzene. If we compare the reactivities of benzene, methylbenzene and nitrobenzene towards nitration reaction, we find the following order:

methylbenzene > benzene > nitrobenzene

i.e., as compared to benzene, methylbenzene is more reactive while nitrobenzene is less reactive. CH_3 group is called an activating group, while NO_2 is a deactivating group for electrophilic substitution of aromatic compounds. By and large, the *meta* directing groups are deactivating and the *ortho* and *para* directing groups are activating, with the exception of halogens.

Let us see if we can explain this on the basis of the intermediate carbocation formed.

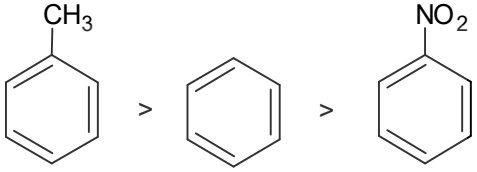


I II III

In the case of methylbenzene (II), the methyl group, which is an electron-donating group, tends to neutralise the charge on the carbocation, this

dispersal of the charge stabilises the carbocation thus leading to faster reaction than benzene.

In case of nitrobenzene (III), the NO_2 group which is electron-withdrawing group, tends to intensify the positive charge and destabilise the carbocation. Due to this effect, the rate of the reaction is slower than in benzene. Reactivity in electrophilic aromatic substitution depends therefore then, upon the tendency of a substituent group to release or withdraw electrons. A group that releases electrons activates the ring while a group that withdraws electrons deactivates the ring. Hence, the order of reactivity of the above compounds towards electrophilic substitution reaction is:

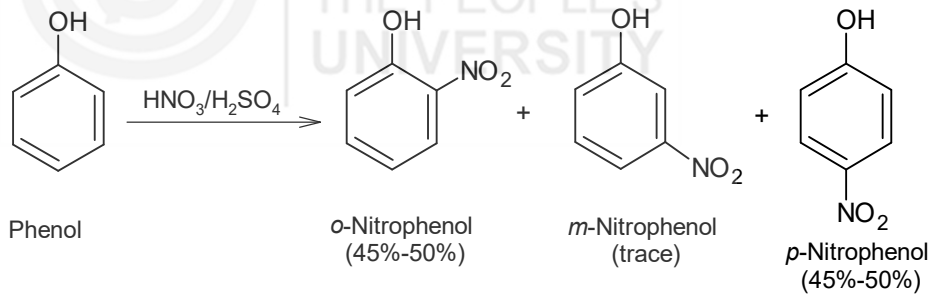


SAQ 1

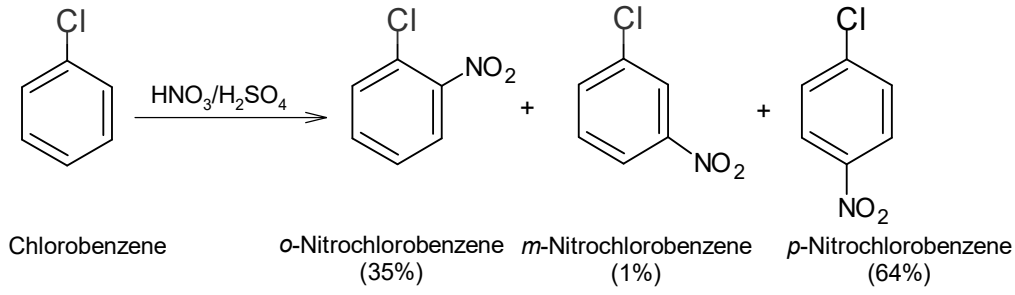
Which compound would you expect to undergo aromatic nitration more readily, C_6H_6 or $C_6H_5CCl_3$ and why?

12.2.3 Effect of Substituents on Orientation

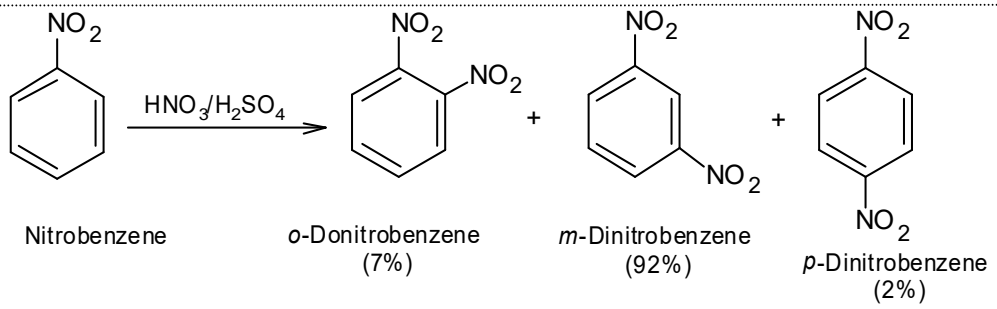
The second effect of a substituent is to direct the position of the incoming substituent. Thus, for instance, nitration of phenol gives *ortho*- and *para*-nitrophenols as major products.



Halogens are unusual in their effect on electrophilic aromatic substitution, we will discuss it under the heading "*ortho* and *para* directing deactivators" of this section . Nitration of chlorobenzenes yields *ortho*-chlorobenzene and *para*-chlorobenzene as the major products.



On the other hand, nitration of nitrobenzene yields *meta*- dinitrobenzene as the major product, i.e.,



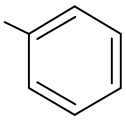
Nitrobenzene | *o*-Donitrobenzene (7%) | *m*-Dinitrobenzene (92%) | *p*-Dinitrobenzene (2%)

This shows that different substituents have different effect on the substitution reaction. Thus substituents can be classified into three the following groups. i.e.

- *ortho* and *para*-directing activators
- *ortho* and *para*-directing deactivators
- *meta*-directing deactivators

Table 12.1 gives a list of substituents with their directive influence and also whether they activate or deactivate the ring.

Table 12.1: Lists some of the groups in each category

***Ortho-* and *para*-directing activators**	***Ortho-* and *para*-directing deactivators**	***Meta*-directing deactivators**
$-NH_2$	$-I$	$-N^+(CH_3)_3$
$-OH$	$-Br$	$-NO_2$
$-OCH_3$	$-Cl$	$-CN$
$-NHCOCH_3$	$-F$	$-COCH_3$
		$-COOCH_3$
		$-COOH$
		$-CHO$
$-CH_3$		

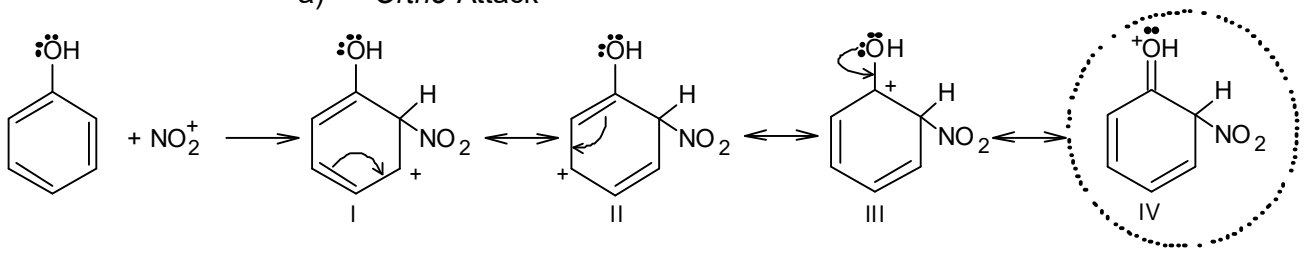
Before we try to account for the orientation in electrophilic substitution, we should clarify our concept of activating and deactivating groups. Remember activating groups activate all the positions of the ring. They are *ortho* and *para* directors because they activate *ortho* and *para* position much more than they do the *meta* position. Similarly, deactivating groups deactivate all positions in the ring. They are *meta* directors because they deactivate the *ortho* and *para* position more than they deactivate *meta* position. Thus, the effect of any group, whether activating or deactivating, is strongest at the *ortho* and *para* positions.

Ortho- and *para*-directing activators:

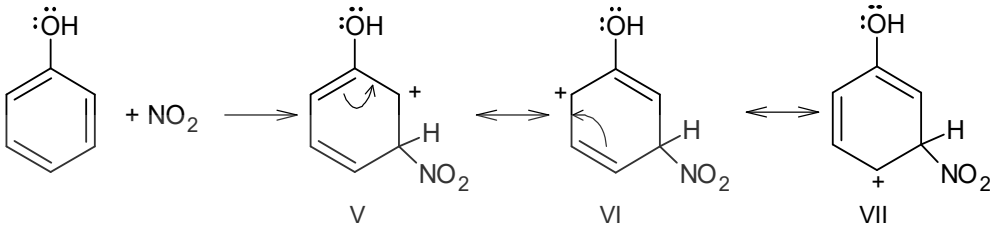
To understand the orientation effect of the substituents, we have to first write all the possible resonance forms of the charged intermediates (carbocations) for each of the three possible reaction courses.

Let us take the example of nitration of phenol. Reaction of NO_2^+ at the *ortho, meta* and *para* positions of phenol gives the intermediate, carbocation with the following resonance structures:

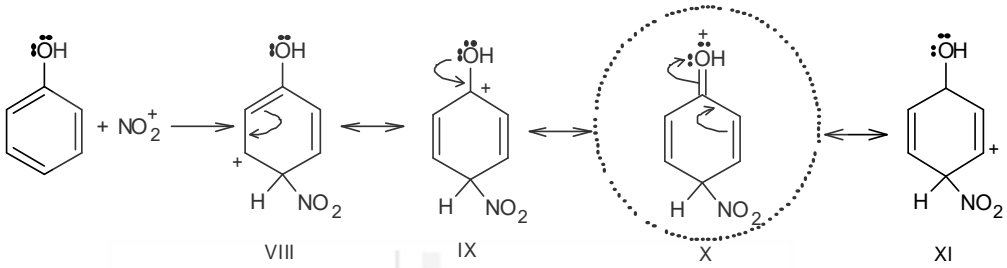
a) *Ortho*-Attack



b) *Meta*-Attack



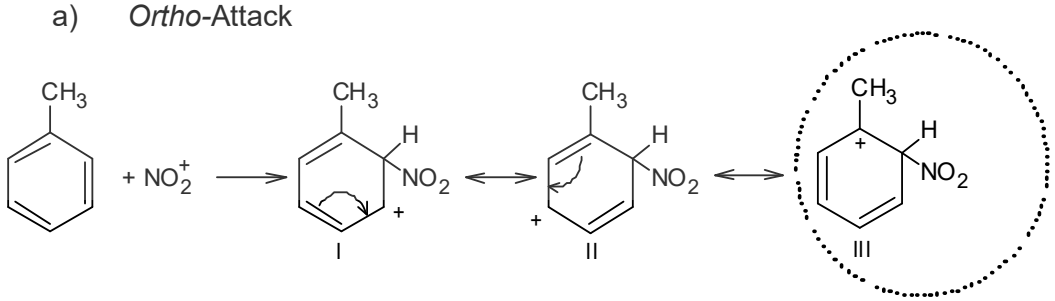
c) *Para*-Attack



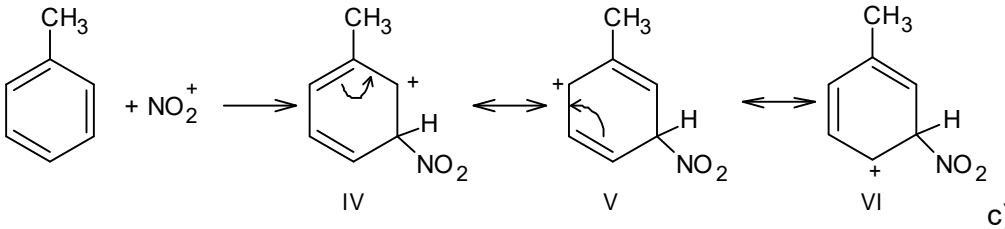
In case of *ortho* and *para* attacks, structures IV and X respectively show that the unshared electron pair of oxygen delocalizes the positive charge of the carbocation and, hence, four resonance structures are possible. In the case of *meta* attack, lone pairs of oxygen are not involved in the delocalisation of positive charge. Hence, the carbocation that is formed has only three resonance structures, therefore, *ortho*- and *para*- nitrophenols are the major products.

Now take the example of electrophilic aromatic substitution on alkyl substituted benzene ring. Let us inspect the possible resonance structures of carbocation formed by the attack of the electrophile, NO_2^+, on toluene.

a) *Ortho*-Attack

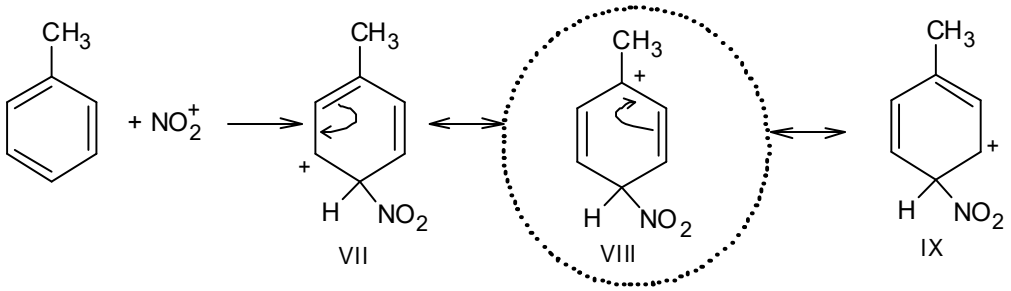


b) *Meta*-Attack



c)

Para-Attack



As indicated above, in structures III and VIII, resulting from *ortho* and *para* attacks respectively, the positive charge is located on the carbon atom to which the methyl group is attached. Because that structure has tertiary carbocation character, it is more stable than the others' in which the positive charge is at a secondary carbocation. On the other hand, *meta* attack produces an intermediate in which none of the resonance structures benefits from such tertiary carbocation stabilisation. Thus, electrophilic attack on a carbon located *ortho* or *para* to methyl group leads to a cationic intermediate that is more stable than the one derived by attack at the *meta* carbon. Substitution at *ortho*- and *para*-position is, therefore, preferred to the *meta*-substitution.

This can also be explained on the basis of inductive effect. The carbocations III and VIII formed by the *ortho*- and *para*-attacks respectively are stabilised by inductive effect of methyl group and are therefore, formed in major amount.

Let us understand this on the basis of potential energy diagram for nitration of methylbenzene (Fig. 12.1). The carbocations formed from attack at *ortho* and *para* positions of toluene are more stable than the carbocation formed from *meta* position. However, all the three carbocations obtained from methylbenzene are more stable than the carbocation obtained from benzene.

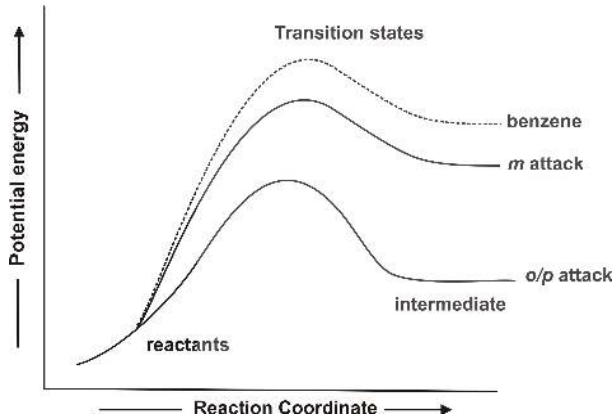
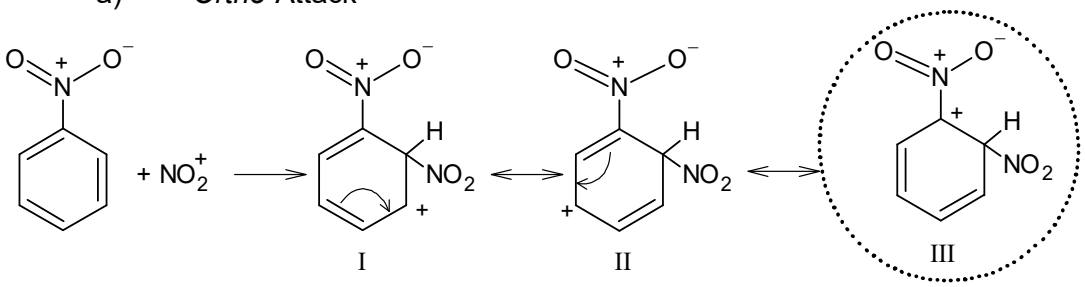


Fig. 12.1: Schematic potential energy diagram for AESR in benzene (----------) and methylbenzene (———)

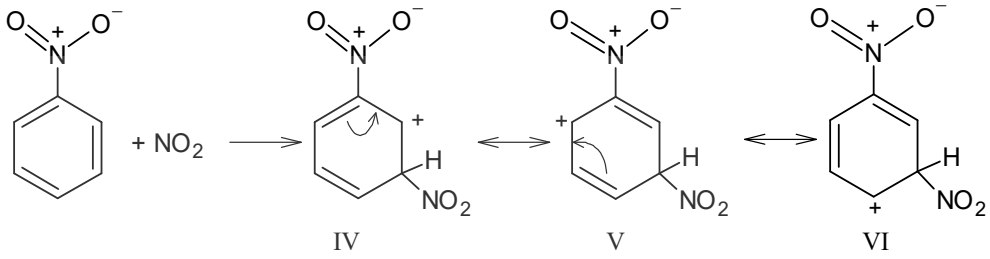
Meta-directing deactivators:

We can apply similar arguments to *meta*-directing groups. These groups are all electronegative groups without an unshared electron pair on an atom adjacent to the benzene ring. In all these cases, the benzene ring would be deactivated. Let us take the example of nitration of nitrobenzene. The possible resonance structures of the carbocation formed are as follows:

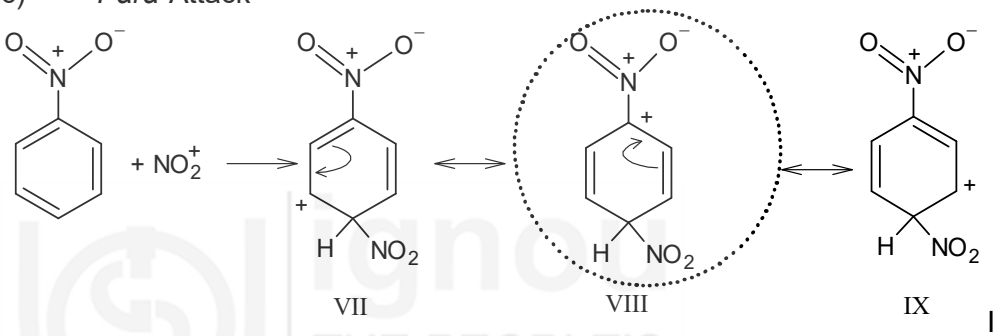
a) *Ortho*-Attack



b) *Meta*-Attack



c) *Para*-Attack



In all the three cases, carbocations formed have three resonance structures. But the structures III and VIII resulting from *ortho* and *para* attack, respectively, are very unfavourable because the positive charge is placed directly on the carbon carrying the electron withdrawing group. A severe electrostatic repulsive interaction between the carbocation and the positive end of the NO_2^+ group strongly disfavours these carbocations. However, the carbocations formed by *meta* attack, have no such form with similar charges on adjacent atoms. Therefore, its transition state is the most stable, and attack at *meta*-position is preferred. Potential energy diagram of the reaction is shown in Fig. 12.2. The carbocation obtained from *meta* attack is more stable than the *ortho* and *para* attack.

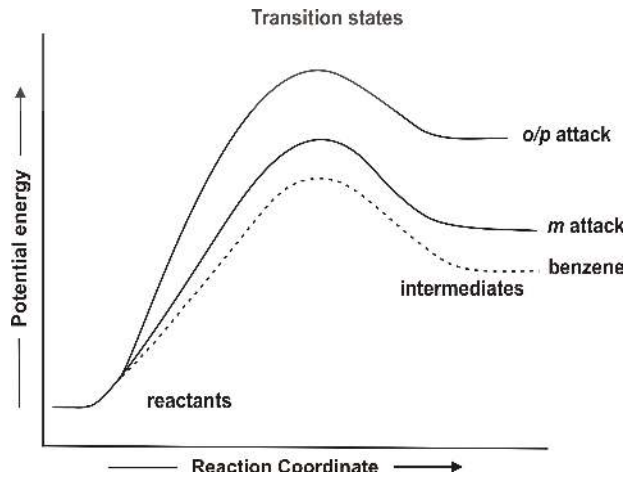
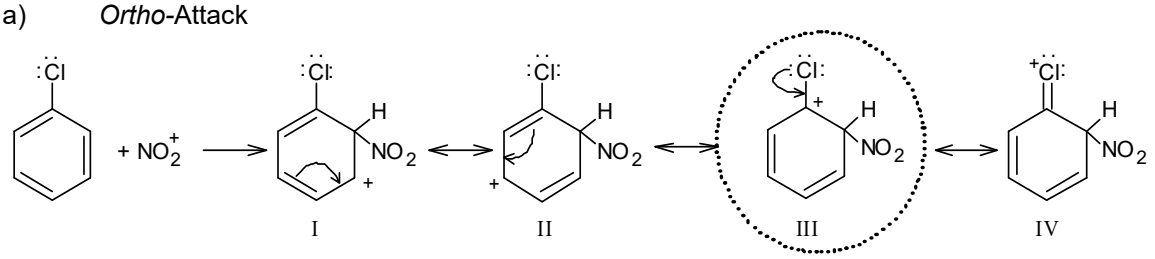


Fig. 12.2: Schematic potential energy diagram for AESR in benzene (-----) and nitrobenzene (——)

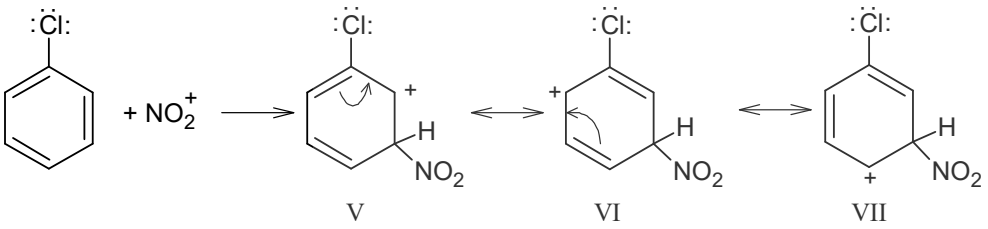
***Ortho* and *para* directing deactivators:**

Halogens are unusual in their effect on electrophilic aromatic substitution. They are deactivating yet *ortho* and *para* directing. For understanding the orientation, consider the attack of electrophile at *ortho*, *meta* and *para* position of chlorobenzene.

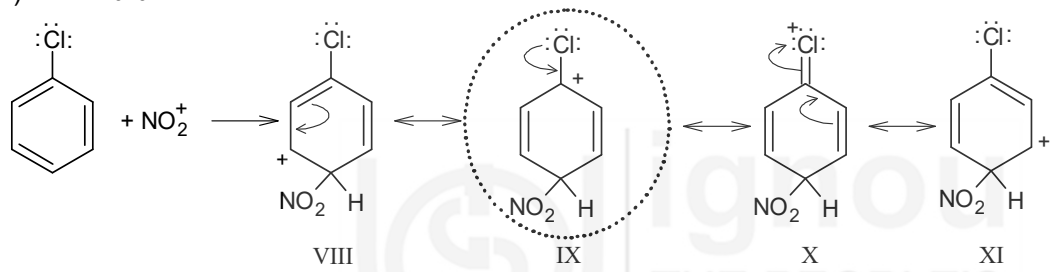
a) *Ortho*-Attack



b) *Meta*-Attack



c) *Para*-Attack



In structures, III and IX, resulting from *ortho* and *para* attacks respectively, there is a positive charge on carbon bearing the halogen atom. Through its inductive effect, chlorine withdraws electrons, making this structure unstable. But there is another factor that one should not forget. It is known that halogens can share a lone pair of electrons and accommodate the positive charge, as shown in structures IV and X, for *ortho* and *para* attacks, respectively. These structures are comparatively stable. No such structure is possible when the electrophiles attack on *meta* position. Structures IV (in *ortho* attack) and X (in *para* attack) outweigh the instability rendered by structures III and IX. Therefore, attack at *ortho* and *para* position is preferred. The potential energy diagram of this reaction is shown in Fig. 12.3. The carbocation obtained from *ortho* and *para* attack is more stable than the carbocation obtained from attack at *meta* position.

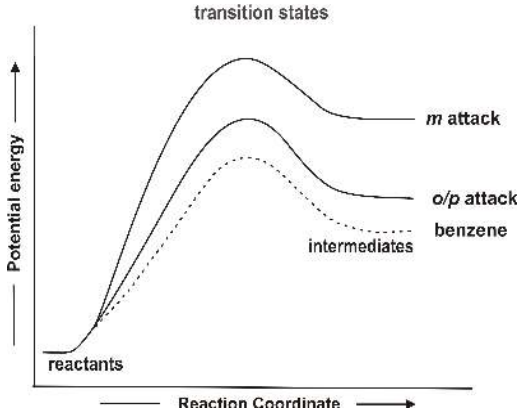


Fig. 12.3: Schematic potential energy diagram for AESR in benzene (----------) and chlorobenzene (———)

SAQ 2

Predict the major and minor products of the following reactions:

a) Nitration of bromobenzene

b) Nitration of nitrobenzene

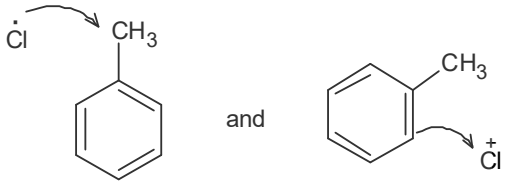
c) Bromination of nitrobenzene

d) Chlorination of pheno

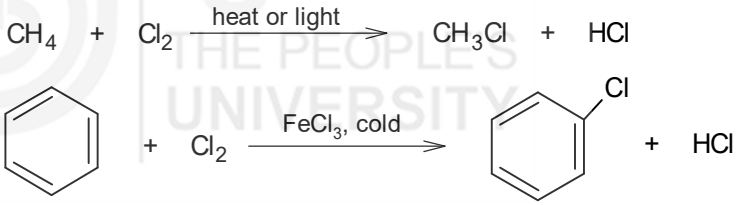
12.3 REACTIONS OF SIDE-CHAIN

12.3.1 Substitution in the Side Chain

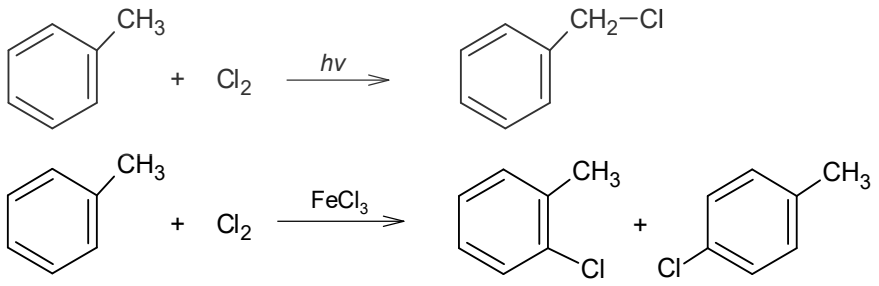
Alkylbenzene clearly offers two position for attack by halogen: the ring and the side chain.



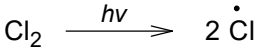
We can control the position of attack by choosing the proper reaction conditions. Halogenation of an alkane requires condition under which halogen atoms are formed by homolyses of halogen molecules, that is, high temperature or light. Halogenations of benzene, on the other hand, involve transfer of positive halogen, which is promoted by Lewis acid catalyst like ferric chloride.

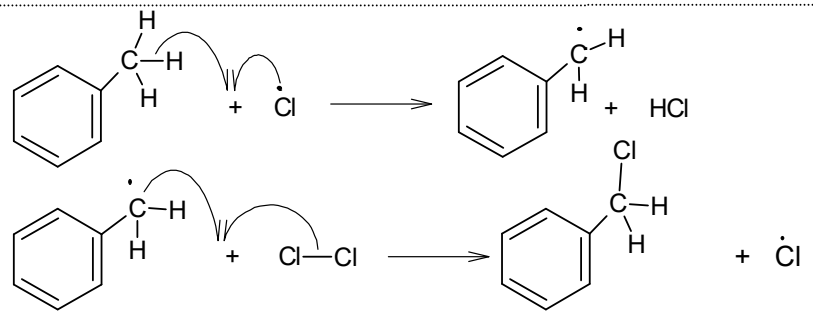


The position of attack in methylbenzene (toluene) would be decided by the nature of the attacking particle and by the condition employed. If the reaction is carried out in the presence of light, substitution occurs almost exclusively in the side chain. In the absence of light and in the presence of ferric chloride, substitution occurs mostly in the ring, for example:

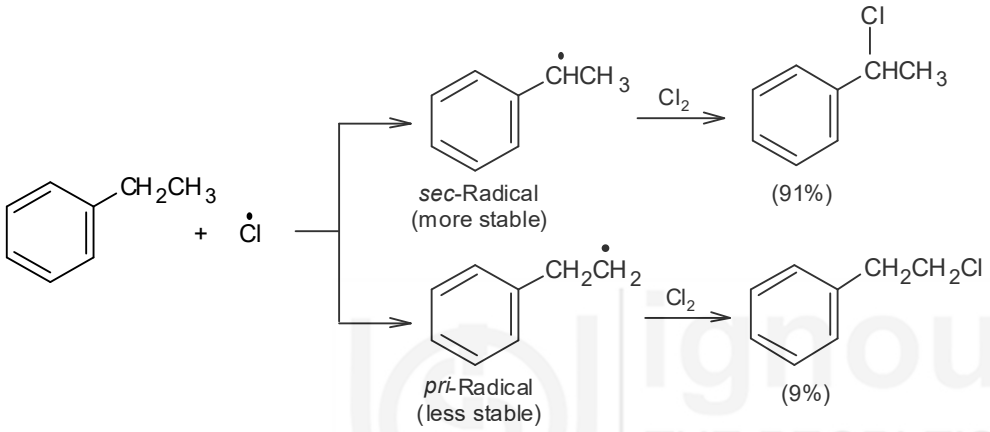


Chlorination of methylbenzene (toluene), in the presence of light, takes place *via* free radical chain mechanism as shown below:

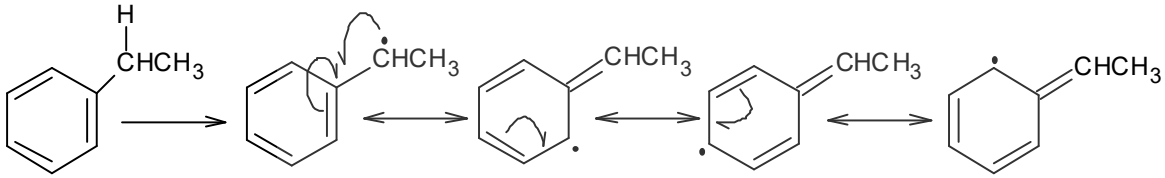




In alkylbenzenes, with side chains larger than methyl, it is expected that the free radical substitution may take place on any of the side chain carbon atoms; so we must consider the likelihood of obtaining a mixture of isomers. For example, chlorination of ethylbenzene should give two isomeric products, 1-chloro-1-phenylethane and 2-chloro-1-phenylethane in equal amounts. But 1-chloro-1-phenylethane is the major (91%) product becouse of the stabilisation of free radical intermediate.



You can ask, why is it so? This is because the bond dissociation energy of benzylic C—H bond, $C_6H_5CH(CH_3)H$, (355 kJ mol^{-1}) is less than β-phenyl ethyl C—H bond, $C_6H_5—CH_2CH_2—H$ (435 kJ mol^{-1}). That means, less energy is required for the homolylic fission of benzylic C—H bond. In other words, benzyl radical is more stable. The greater stability of benzyl radical is due to delocalisation of the odd electron over the ring as shown below:



Since the benzylic radical formed is more stable, 1-chloro-1-phenylethane is the major product.

SAQ 3

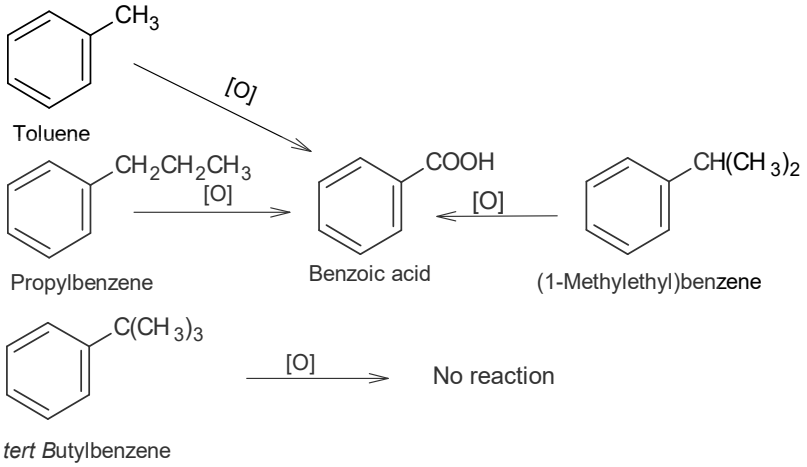
Write the mechanism of chlorination of methyl benzene.

12.3.2 Oxidation of Side-chain

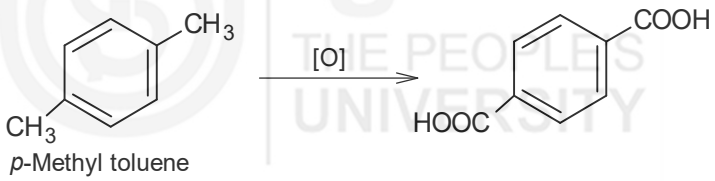
Although benzene is quite unreactive towards the usual oxidising agents ($KMnO_4$, $K_2Cr_2O_7$ etc.), the benzene ring renders an aliphatic side chain quite susceptible to oxidation. The side chain, irrespective of its length is oxidised to

a carboxyl group (−COOH). Tertiary alkyl substituted aromatic compounds do not undergo this reaction. For example, toluene, propylbenzene, (1-methylethyl)benzene are oxidised to benzoic acid in high yields. *p*-Methyltoluene on oxidation gives terephthalic (benzene-1,4-dicarboxylic) acid but tertiary butylbenzene is not effected.

The number and the position of the carboxylic groups produced indicate the number and position of alkyl chain(s) attached to the aromatic ring.

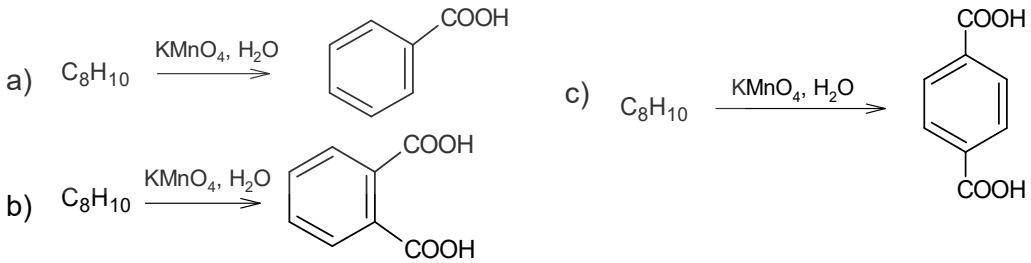


Terephthalic acid is used for the production of polyester fibres in industries. Remember for industrial purposes Terephthalic acid is prepared from *p*-xylene by simple oxidation using air as the oxidant and Co(III) salt as a catalyst .



SAQ 4

Draw the structural formulas for the starting materials in the following reaction:



12.4 SUMMARY

- Alkylbenzenes offer two main areas for attack by halogen–the ring and the side chain.
- In the presence of light, halogen goes to side chain while in the presence of acid catalyst it goes to ring.

- Substituents affect the reactivity and the orientation in the benzene ring.
- A given substituent already attached to the benzene ring usually directs the position of the second substituent.
- There are two types of substituents – one is electron donating group, such as as $-NR_2$, $-OH$, $-OR$, $-NHCOR$, and $-R$ and other is electron withdrawing groups which include halogens, $-CHO$, $-COR$, $-COOR$, $-CN$, $-NO_2$, $-\overset{+}{N}R_3$ etc.
- Besides being different in their 'directing' tendencies,$-CH_3$ and $-NO_2$ groups differ in one more aspect and that is the rate of the reaction. Rate of nitration of benzene, methylbenzene and nitrobenzene is as follows:
- Methylbenzene > benzene > nitrobenzene
- The second effect of a substituent is to direct the position of the incoming substituent. Thus, nitration of phenol gives *ortho* and *para*-nitrophenol as major products. On the other hand, nitration of nitrobenzene yields *meta* dinitrobenzene as the major product,
- This shows that different substituents have different effect on substitution reaction. Thus substituents can be classified into three groups. i.e.,
- *ortho* and *para*-directing activator
- *meta*-directing deactivator
- *ortho* and *para*-directing deactivator
- The side chain, irrespective of its length, is oxidised to a carboxyl group (-COOH).
- Tertiary alkyl substituted aromatic compounds do not follow oxidation reaction.

12.5 TERMINAL QUESTIONS

1) Write equation to show how the following conversion takes place.

   a) Methylbenzene to *m*-bromobenzonic acid

   b) benzene to *p*-nitrotoluene

   c) benzene to *m*-nitrocetophenone

2) Write the chemical equation for the oxidation of the following compounds with hot $KMnO_4$.

   a) *n*-Butylbenzenes

   b) 1,1-Dimethylethyl benzene

   c) 1,3,5-Trymethylbenzene

3) Write the resonance structures of cation formed from $C_6H_5NH_2$ during:

   a) *ortho*-bromination

b) *meta*-bromination

c) *para*-bromination

4) Compound A, B and C are the three isomeric dibromobenzenes. Identify which is *ortho*, *para* and *meta* from the number of mononitration products.

a) Compound A $\xrightarrow{HNO_3/H_2SO_4}$ two mononitration products

b) Compound B $\xrightarrow{HNO_3/H_2SO_4}$ three mononitration products

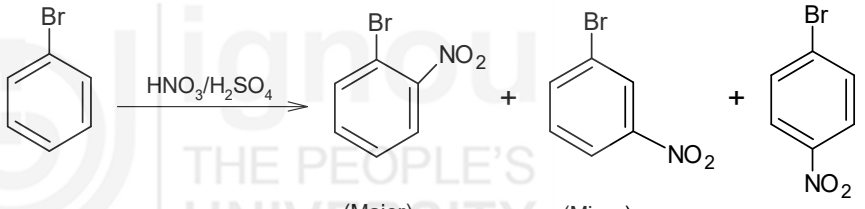
c) Compound C $\xrightarrow{HNO_3/H_2SO_4}$ one mononitration products

12.6 ANSWERS

Self-Assessment Questions

1. While the $-CH_3$ group is electron releasing and activates the ring, the CCl_3 group is strongly electron withdrawing because of the influence of the electronegative chlorine atoms and hence, deactivates the ring. Therefore, $C_6H_5CCl_3$ undergoes substitution more slowly.

2. a)



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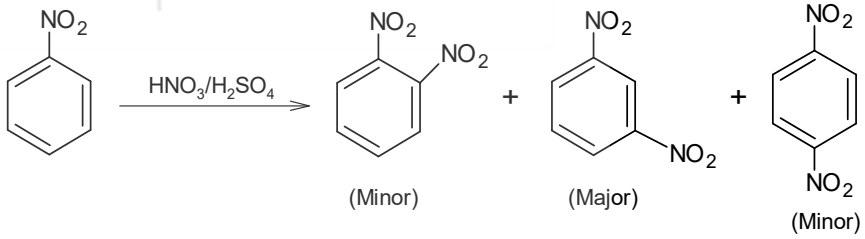

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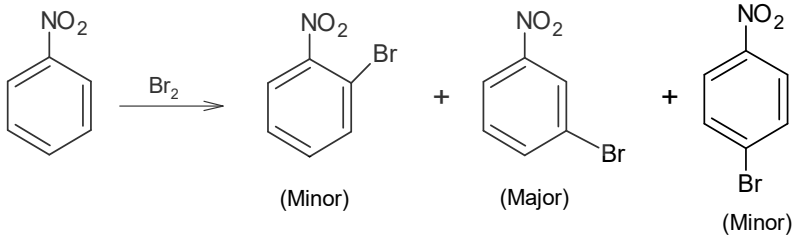

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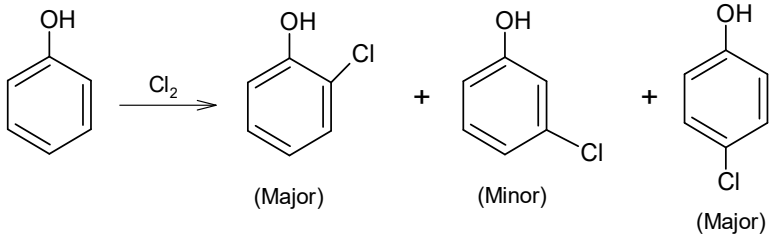
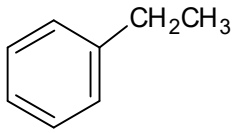
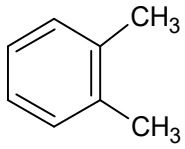
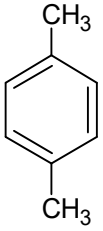


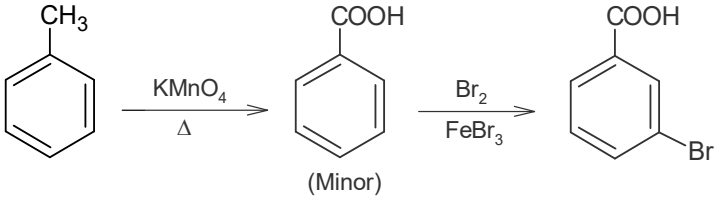
3. See Sub-Sec. 12.3.1

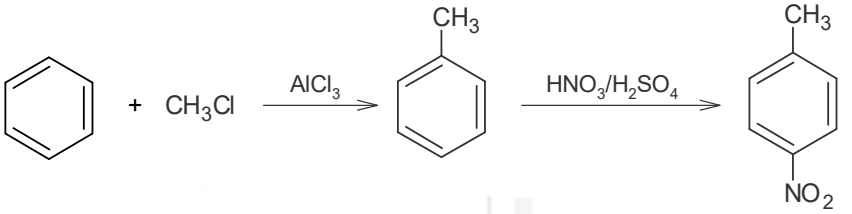
4. a) 

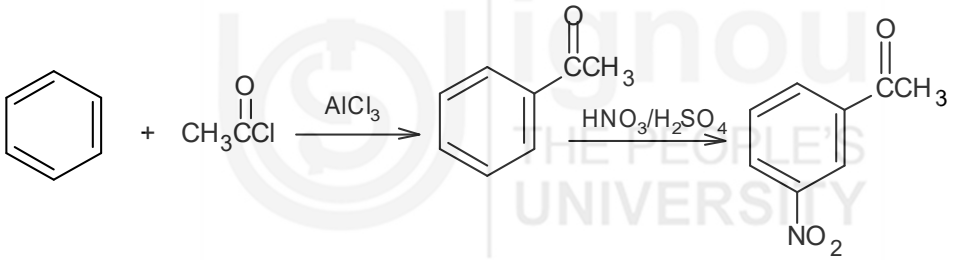
b) 

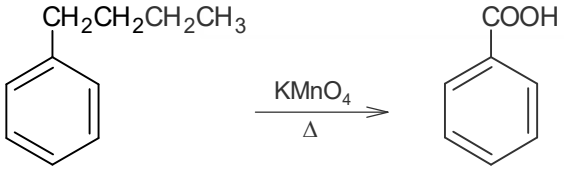
c) 

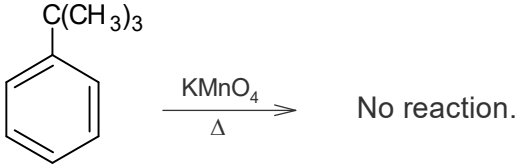
Terminal Questions

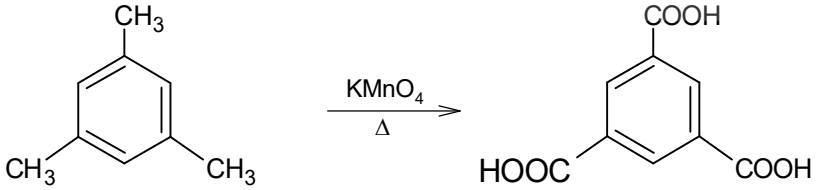
1. a) 

b) 

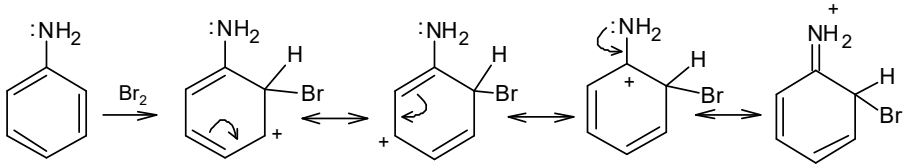
c) 

2. a) 

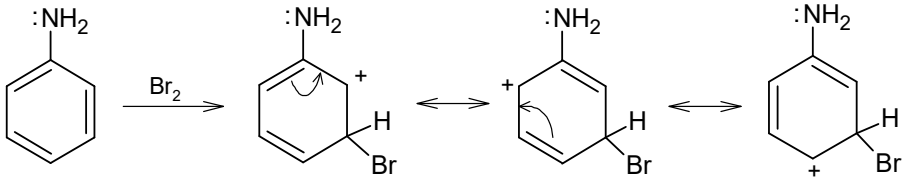
b) 

c) 

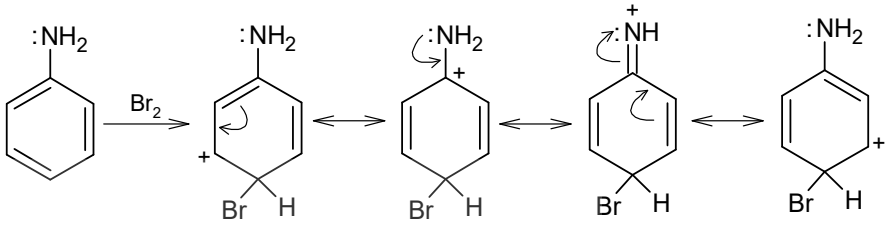
3. a) *Ortho*-Attack



b) *Meta*-Attack



c) *Para*-Attack



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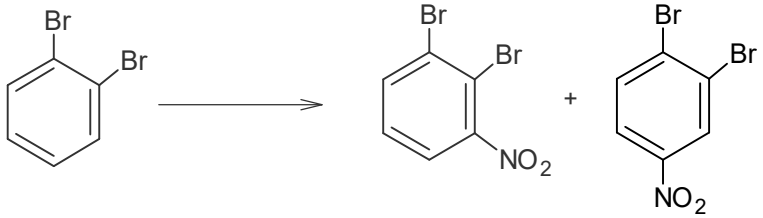
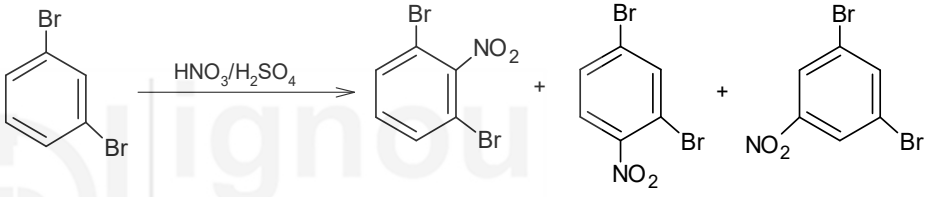


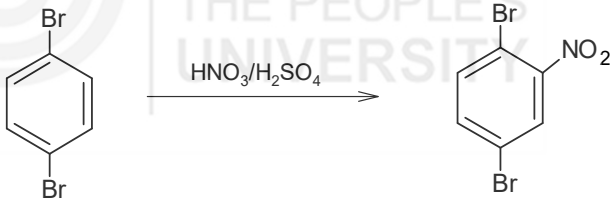
Only these two products are possible from *o*-dibromobenzene

b)



Three products are possible from *m*-dibromobenzene

c)



Only one product is possible from *p*-dibromobenzene

On the basis of above reactions, we can say that:
Compound A is a *o*-dibromobenzene
Compound B is a *m*-dibromobenzene
Compound C is a *p*-dibromobenzene.